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21) International Application Number: PCT/FI92/00081 22) International Filing Date: 23 March 1992 (23.03.92) 30) Priority data: 912262 9 May 1991 (09.05.91) FI 71) Applicant (for all designated States except US): NESTE OY [FI/FI]; P.O. Box 310, SF-06101 Porvoo (FI). 72) Inventors; and 75) Inventors/Applicants (for US only): GAROFF, Thomas [FI/FI]; Borgströminkuja 4 K 104, SF-00840 Helsinki (FI). LEINONEN, Timo [FI/FI]; Hamarin koulu, SF-06650 Hamari (FI). IISKOLA, Eero [FI/FI]; Linnankoskenkatu 15 A 1, SF-06100 Porvoo (FI).	(74) Agent: BERGGREN OY AB; P.O. Box 16, SF-00101 Helsinki (FI). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i> <i>With amended claims.</i>	

54) Title: A PROCATALYST FOR POLYMERIZATION OF OLEFINS CONTAINING A TRANS-ESTERIFICATION PRODUCT OF A LOWER ALCOHOL AND A PHTHALIC ACID ESTER

57) Abstract

In the invention a procatalyst composition intended for the polymerization of olefins has been provided, which has been prepared by bringing together magnesium chloride, a lower alcohol, a titanium compound and an ester of phthalic acid. The procatalyst composition is active and stereospecific and it simultaneously has a titanium and phthalic acid content as low as possible. These good properties have been achieved by carrying out a trans-esterification between the lower alcohol and the ester of the phthalic acid, whereby the alkoxy group of the phthalic acid comprises at least five carbon atoms.

A procatalyst for polymerization of olefins containing a transesterification product of a lower alcohol and a phthalic acid ester.

The invention relates to a procatalyst composition intended for the polymerization of olefins, which has been prepared by bringing together $MgCl_2$, a lower alcohol, a titanium product and an ester of phthalic acid. The invention also relates to the use of said procatalyst composition for the polymerization of propylene.

Olefins, especially α -olefins, are often polymerized by the aid of a catalyst composition, in which the procatalyst is formed by a compound of a transition metal of the groups IV-VI of the periodic table and a compound of a metal of the groups I-III of the periodic table, activating it by reduction, i.e. the co-catalyst. The so-called Ziegler-Natta-procatalyst has been further developed by using as the support of the transition metal an inert carrier, to which the transition metal compound is layered with the intention to thus improve the activity of the procatalyst when it is catalyzing the polymerization reaction.

Yet, influenced by this procatalyst composition, the asymmetrical olefin monomers often polymerize to various kinds of stereoisomeric polymers to form mixtures of e.g. isotactic, atactic and syndiotactic polymers, from which the desirable stereoisomer must be separated by means of often troublesome washing and other stages. When mainly a polymer of a certain stereospecific form is wished to be produced, e.g. an isotactic polyolefin from an asymmetrical olefin monomer, the influence of the catalyst to the stereospecificity has been improved by adding a donor compound to the catalyst. Because of a certain steric structure the donor compound contributes to the settling of the monomer molecule in a certain position in the catalyst particle at the end of the growing polymer molecule, thus giving the molecule chain of the polymer a certain stereoisomeric

amines, organic phosphorus and silicon compounds, etc. These compounds also have other influences on the properties of the catalyst, e.g. the activity of the catalyst varies depending on the donor used. If the donor is an ester of carboxylic acid, usual are the esters of aromatic carboxylic acids, e.g. benzoates, phthalates, toluates, anisates, etc. The most preferable of these donors are the dialkyl phthalates.

Combinations of various donors are also known in the field. Thus, from the JP publications 59172507, 59206409, 59206415, 59206416, 59206424, 60262804, 61103910 and 61108614 is known a procatalyst composition, which is prepared from $MgCl_2$, 2-ethylene hexyl alcohol, titanium tetrachloride, di-isobutyl phthalate and in some cases from phthalic acid anhydride.

The patent family comprising the publications DE 3,540,699, EP 226,003 and US 4,761,461, discloses a procatalyst composition, which has been obtained by bringing together $MgCl_2$, alcanol, such as ethanol, an ester of phthalic acid, such as di-isobutyl phthalate, and titanium tetrachloride in certain conditions. The ester of phthalic acid can be added either at the stage when $MgCl_2$ and ROH are reacting with each other, or at the stage when the reaction product of $MgCl_2$ and alcanol are brought to react with titanium tetrachloride.

The high titanium content of the above-mentioned procatalysts causes colour problems in the polymers and the high phthalic acid content brings forth non-desirable aromatic residues in the polymers.

The aim of the invention is the provision of an active and stereospecific procatalyst composition, which simultaneously has a titanium and phthalic acid content as low as possible. The aim has now been achieved by the new procatalyst composition intended for the polymerization of olefins, which is mainly characterized by what is stated in the characterizing clause of Claim 1. It has, thus, been realized that when preparing a procatalyst composition by

Also other transition metal compounds, such as vanadium, zirconium, chromium, molybdenum, and tungsten compounds, can be mixed with the titanium compound, if necessary. The titanium compound usually is halide or oxyhalide, an organic metal halide, or a purely metal organic compound, in which only organic ligands have been attached to the transition metal. Particularly preferable are the titanium halides, expressly TiCl_4 .

The alkoxy group of the phthalic acid ester used comprises at least 5 carbon atoms. As the above-mentioned good properties become accentuated when the alkoxy group becomes longer, it is advantageous if the alkoxy group of the phthalic acid ester comprises at least 8, and preferably 10 carbon atoms. Thus, among others propylhexyl phthalate (PrHP), in the alkoxy group of which there are 6 carbon atoms, dioctyl phthalate (DOP), in the alkoxy group of which there are 8 carbon atoms, di-isodecyl phthalate (DIDP), in the alkoxy group of which there are 10 carbon atoms, and ditridecyl phthalate (DTDP), in the alkoxy group of which there are 13 carbon atoms, can be used as the ester. The molar ratio of phthalic acid ester and magnesium halide is in the synthesis preferably of the size class about 0.2.

It is also preferable if the ester of the phthalic acid used acts as the so-called electron donor of the catalyst composition with the intention to improve the activity and the stereospecificity of the polymer.

The transesterification can be carried out e.g. by selecting a phthalic acid ester - a lower alcohol pair, which spontaneously or by the aid of a catalyst, which does not damage the procatalyst composition, transesterifies under normal preparation conditions of the catalyst. Often it is, however, necessary to use an elevated temperature in order to achieve transesterification. Hereby, it is preferable to carry out the transesterification at a temperature which is between 110-150° and preferably between 130-140°C.

obtained, in which the group derived from the alcohol of the ester has been exchanged:



If enough titanium remains on the carrier, it acts as an active part of the procatalyst. Otherwise, a new titanification is carried out after the above-mentioned treatment in order to ascertain a high enough titanium content and thus activity. The titanium separation of the formula (4) mainly concerns with the inactive part of the titanium.

Thus, in the present invention a procatalyst composition intended for the polymerization of olefins has been achieved, the titanium and donor contents of which are low in regard to the activity of the catalyst. The procatalyst composition contains according to one embodiment 2.5% by weight of titanium at the most and preferably 2.0% by weight of titanium at the most. Its molar ratio donor/Mg preferably is between 0.03-0.06 and/or its donor content is between 4 to 6% by weight. According to one embodiment of the invention the alcoxy group of the phthalic acid comprises at least 8 carbon atoms and the activity of the procatalyst composition when triethyl aluminum is used as the catalyst and cyclohexylmethyl dimethoxy silane is used as the outer donor is at least about 800kg PP/g of Ti.

According to the invention the procatalyst composition intended for the polymerization of olefins is preferably prepared by

- a) bringing an adduct of MgCl_2 and a lower alcohol to react with TiCl_4 ,
- b) bringing the product of the stage a) to react with an ester of the phthalic acid under conditions where a transesterification takes place between the ester of phthalic acid and the lower alcohol,
- c) washing the product,

Table 1The tested internal donors

Test	Length of the alkyl group	Donor	Molar mass g/mole	Density g/ml
1	4	DIBP	278	1.00
2	6	PrHP	292	0.95
3	8	DOP	390	0.96
4	10	DIDP	446	0.96
5	13	DTDP	530	0.91

Catalyst synthesis

0.1 mole of $\text{MgCl}_2 \cdot x \text{ EtOH}$ was suspended under inert conditions into 250ml of decane in a reactor. The solution was cooled to the temperature of -15°C and 300ml of cold TiCl_4 was added. Then a controlled heating to the temperature of $+20^\circ\text{C}$ was carried out. At this temperature 0.02 mole of the internal donor was added. In all the catalyst syntheses the molar ratio between the donor and the MgCl_2 was 0.2. When all the synthesis reagents were present, the temperature was raised to 135°C . Both the first and the second titanification was carried out at this temperature. The catalyst synthesis was ended by carrying out a wash for the reaction mixture.

In order to find out the particle size of the procatalyst produced the particle size distribution was measured out and microscope pictures were taken of each sample. Moreover, the chemical composition of the procatalysts was measured by analyzing their Ti, Mg and donor contents. Also X-ray diffraction spectra were taken for the examination of the changes taking place in the crystal structure.

Test polymerization

For all the catalysts a test polymerization was carried out under the following polymerization conditions. As the reaction vessel was used a 2-liter bench reactor. In the test polymerization 20 to 30g of procatalyst was used. This

Table 2The symbols of the catalysts and polymers used in the test

<u>Length of the alkali group</u>	<u>Symbol of the catalyst</u>	<u>Symbol of the polymer</u>
4	C-C-4	1 PP-C-4
6	C-C-6	2 PP-C-6
8	C-C-8	3 PP-C-8
10	C-C-10	4 PP-C-10
13	C-C-13	5 PP-C-13

The titanium content of the catalyst

The magnesium and titanium contents of the catalyst are shown in table 3. The titanium content has also been disclosed in fig. 1. The results shew that when the Mg-content remained substantially unchanged a systematic decrease of the Ti-content was observed in the catalyst series. The longer was the alkyl chain of the electron donor's alkoxy group, the smaller was the Ti-content of the final procatalyst. The Ti-content of the last catalyst of the series was 1.6% by weight. This is a 60% smaller value than the 4% value which was achieved in the standard synthesis and even 30% lower than the titanium content found in commercial high-yield catalysts. These results shew that the combination of transesterification and the washing effect of $\text{TiCl}_3 \cdot x \text{OEt}$ worked better when higher phthalic acid esters were used.

Table 3The Mg- and Ti-content of the catalysts

<u>Length of the alkyl chain</u>	<u>Mg (%)</u>	<u>Ti (%)</u>
4	18.1	2.4
6	20.8	2.2
8	22.0	1.9
10	20.0	1.9
13	17.3	1.6

catalysts was about constant and close to 5%. This corresponds to the D/Mg ratio 0.03 to 0.04 (D = donor), which is even a lower value than what was achieved when DIBP was transesterificated at the temperature of 143°C.

These results show that the transesterification improves if longer alkyl chains are used in phthalic acid esters. It appears simultaneously that a low electron donor/MgCl₂ molar ratio is achieved.

Table 5

The donor composition of the catalysts. PA = acid anhydride and IE = mixed esters produced during the transesterification

Length of the alkyl group	Original (%)	DEP (%)	PA (%)	IE (%)
4	3.6	4.0	1.3	1.0
6	0.2	5.3	0.3	0.9
8	0.3	4.8	0.7	0.4
10	0.4	5.3	1.1	0.5
13	0.2	5.9	0.7	0.4

The particle size distribution (PSD) of the catalysts

Also the PSD of the catalysts was measured and the results are shown in table 6. In fig. 4 there has been presented the average particle diameter of the portion which comprised over 90% of the particles as a function the length of the donor's alkyl chain. The results show that when the donor composition changes also the PSD changed greatly.

Simultaneously, it could be noted that the catalyst particles agglomerated when higher phthalic acid esters were used. This agglomeration can be seen in the PSD-curves of the figures 5, 6, and 7 and in the microscope pictures of figures 8, 9, and 10. The results also shew that the agglomeration decreased a little with higher phthalic acid esters. By using DIDP (C = 10) catalyst particles with a very beautiful shape were obtained, the diameter of which was about 140µm. This appears from figure 10.

The surface area and the pore volume of the catalysts

From the catalysts were measured both the surface area and the pore volume. The results have been listed in table 8. According to the results the surface area of the catalysts remained nearly unchanged independent on the donor used in the synthesis. The specific surface achieved was of the size class about 300m²/g. The pore volume, on the other hand, grew when transferring into donors with longer chains. In the last catalyst of the series an increase of as much as 60% was observed. The growth of the pore volume can partly be explained by the agglomeration of the catalyst particles.

Table 8The specific surface area and the pore volumes of the catalysts

Length of the alkyl group	Surface area (m ² /g)	Pore volume (ml/g)
4	348	0.524
6	316	0.738
8	311	0.581
10	339	0.776
13	292	0.814

Activity of the catalysts

All the catalysts were test polymerized in the above-mentioned conditions. The results have been presented in table 9 and figure 13. The activity based on the weight of the catalyst and the polymer remained constant for the whole catalyst series and was about 16kg/g cat. When expressed in unit kg PP/g Ti the activity systematically. This was due to the fact that the Ti-content decreased correspondingly when transferring into higher phthalic acid esters. Thus, the activity value 1019kg PP/g Ti was obtained for the last catalyst of the series. When decane was used as the activation medium the activity of the catalyst was a little smaller.

The bulk density of the polymers

The bulk density decreased when higher phthalic acid esters were used in the transesterification synthesis. The results have been listed in table 11 and presented in figure 18.

Table 11The bulk density of the polymers

<u>Length of the alkyl group</u>	<u>Bulk density (g/ml)</u>
4	0.46
6	0.44
8	0.33
10	0.37
12	0.39

The melt index of the polymers

The chain length of the ester did not have much significance for the melt index. The results have been presented in table 12.

Table 12The melt index of the polymers

<u>Length of the alkyl group</u>	<u>Melt index (2.16kg)</u>
4	10.5
6	9.3
8	10.0
10	7.3

Molecular weight of the polymers

No systematic changes of the molecular weight distribution could be observed when the ester changed. All results have been listed in table 13. The results correspond to the results normally obtained in standard polymerization.

Table 13Molecular weight distribution of polymers

Length of alkyl group	Mn	Mw	Mv	D
4	58,000	173,000	223,000	4.7
4	58,800	274,000	222,000	4.7
6	56,000	281,000	225,000	5.2
6	55,200	289,000	232,000	5.2
8	60,100	273,000	221,000	4.6
8	60,700	279,000	228,000	4.6
10	73,800	331,000	269,000	4.5
10	74,600	334,000	270,000	4.5

The DSC measuring results of the polymers

In table 14 the melting points, the crystallization points and the crystallinity percentages of the polymers have been listed. Neither could it be observed here any systematic dependency of the esters used. The melting point is about 161°C and the crystallizing temperature about 114°C. The crystallinity was about 51-52%. In figures 19, 20, and 21 some melting curves have been presented.

It can generally be said that a correlation prevails between the titanification temperature and the crystallization temperature of the catalyst. A higher titanification temperature gives purer catalyst and more homogeneous polypropene. This, on its part, increases the crystallinity of the polymer and decreases the crystallizing temperature. The correlation between the titanification temperature of the catalyst and the crystallizing temperature of the polymer is schematically presented in figure 22.

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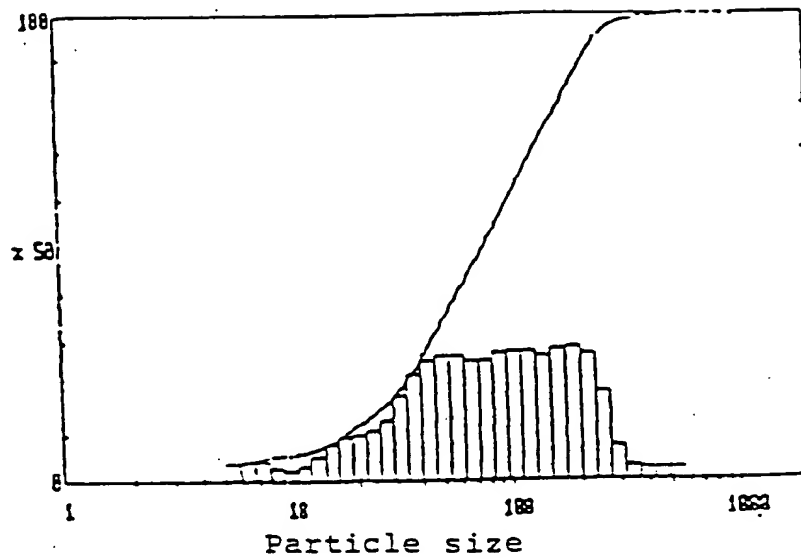


Fig. 5

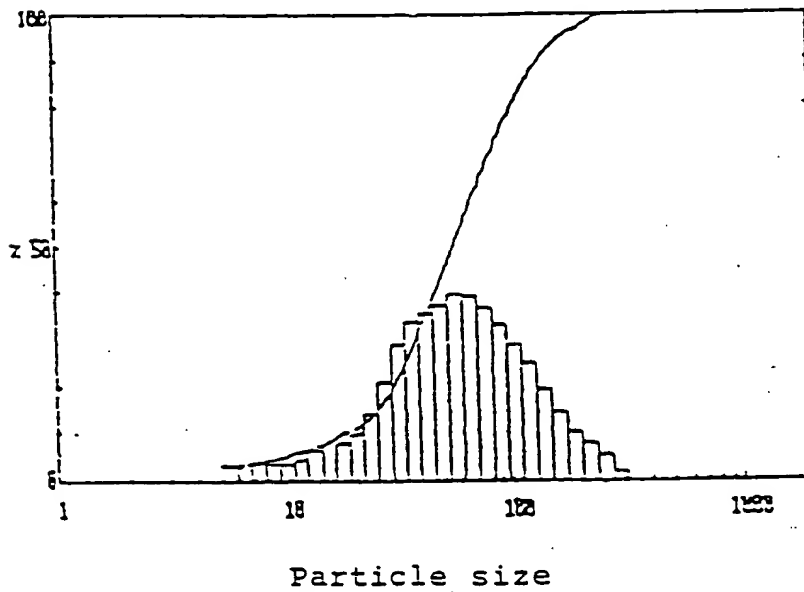


Fig. 6

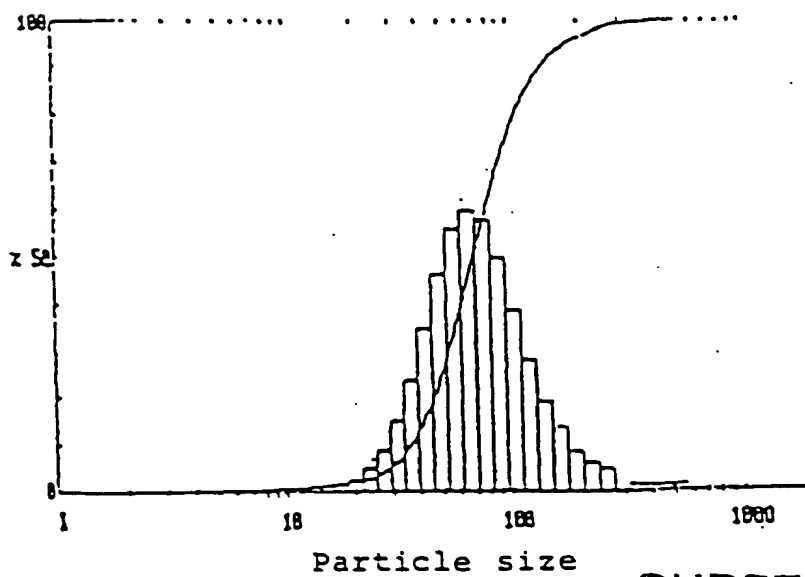


Fig. 7

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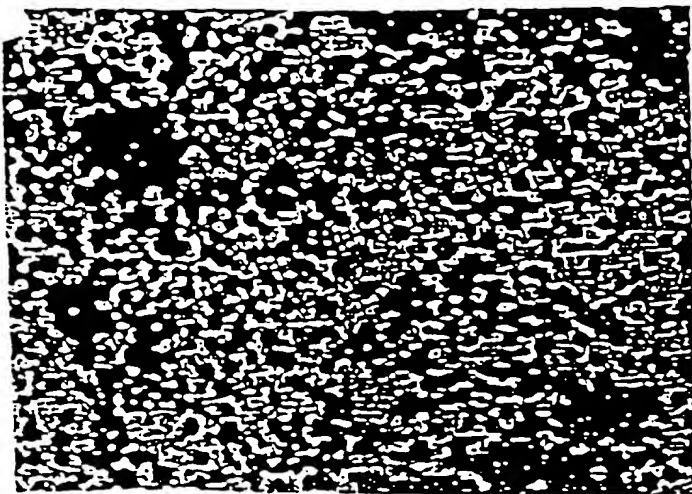


Fig. 8

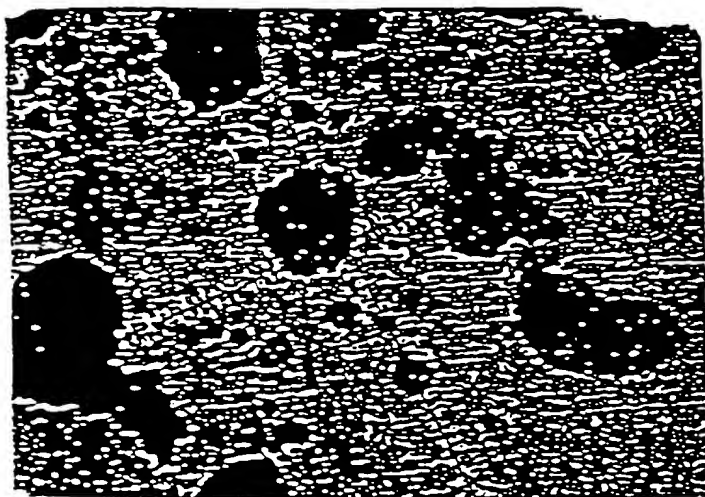


Fig. 9

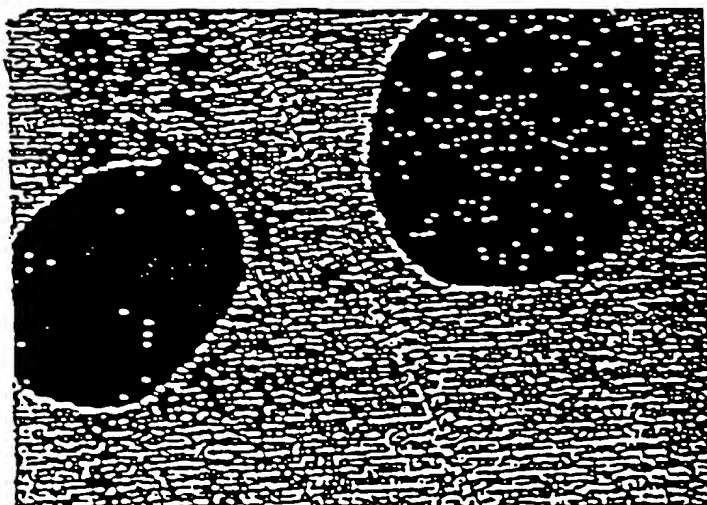


Fig. 10

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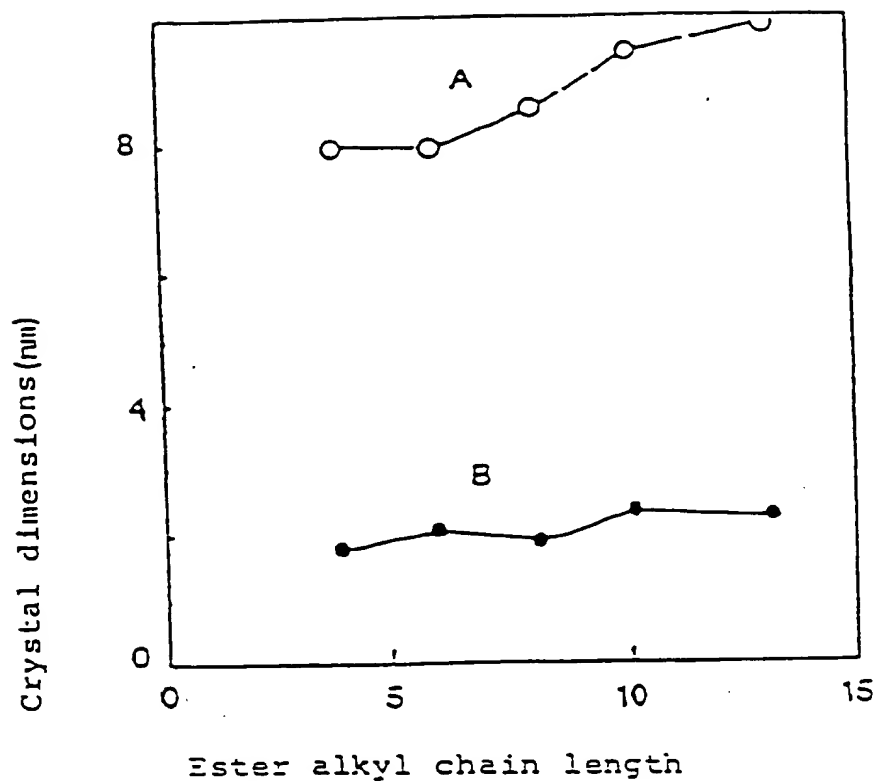


FIG. 11

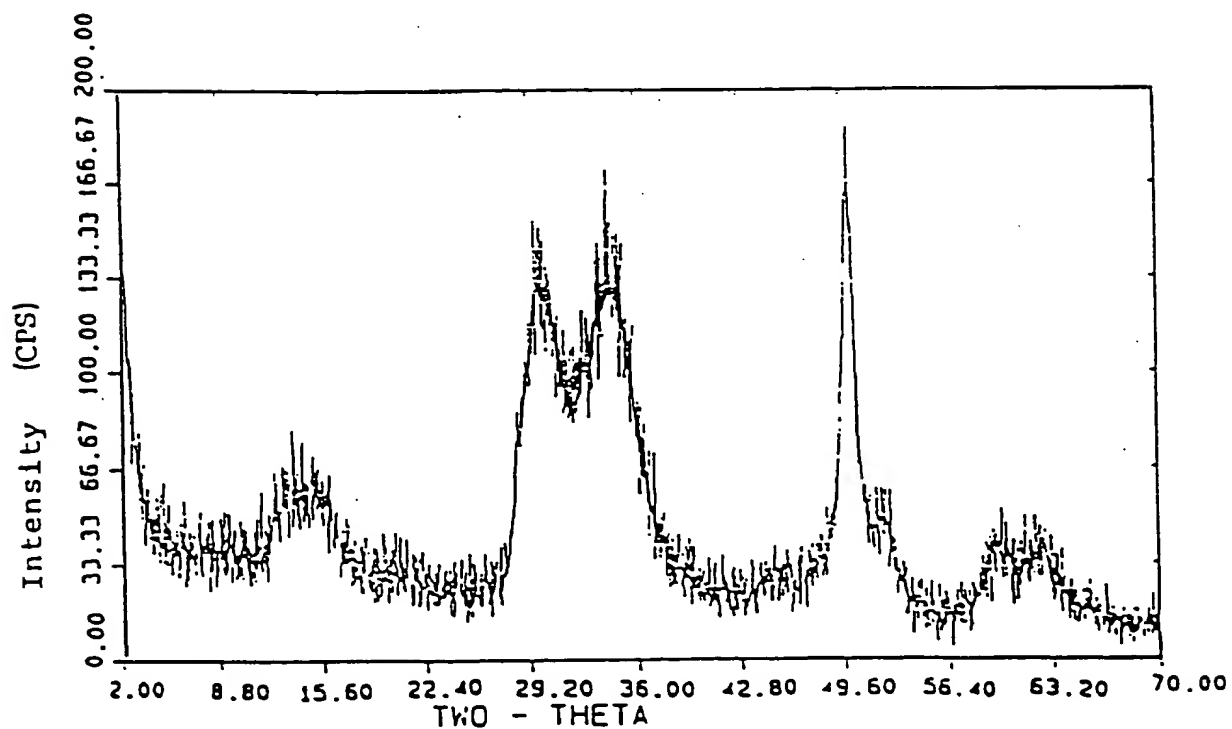


FIG. 12

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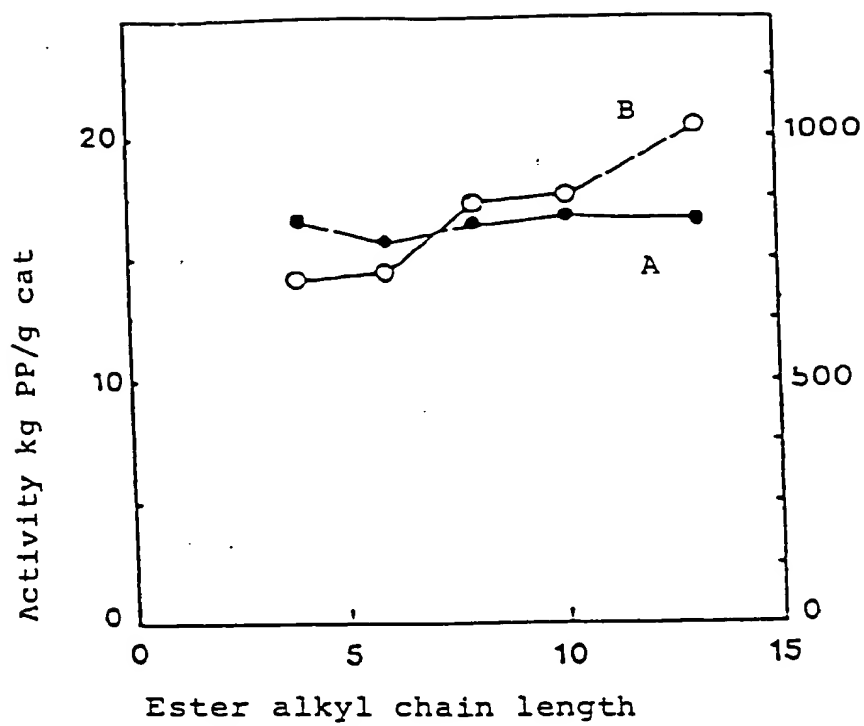


FIG. 13

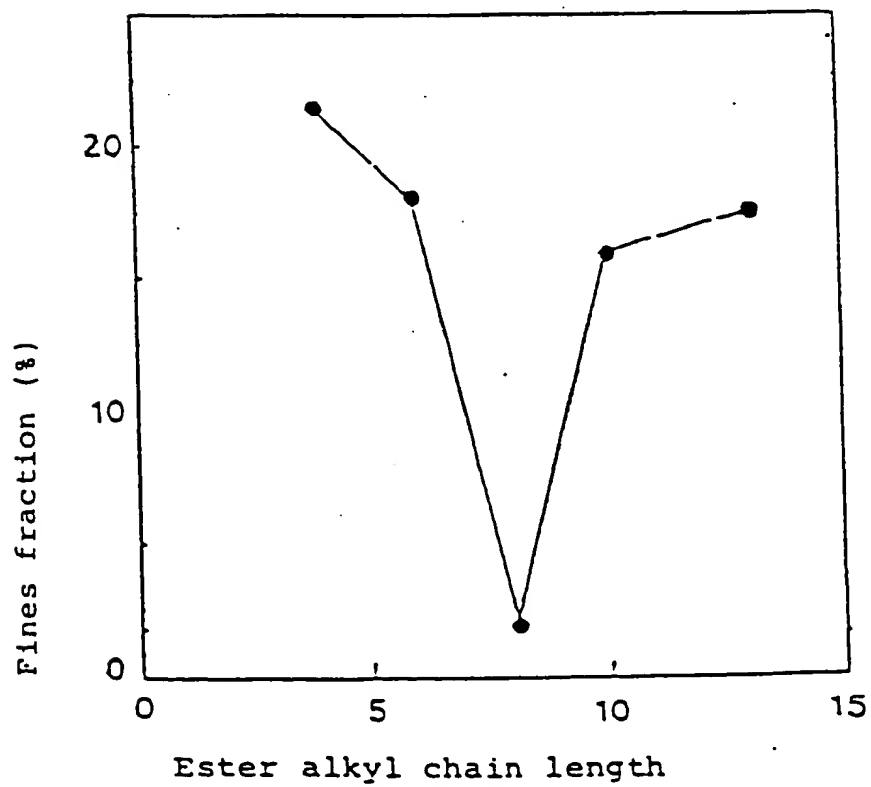


FIG. 17

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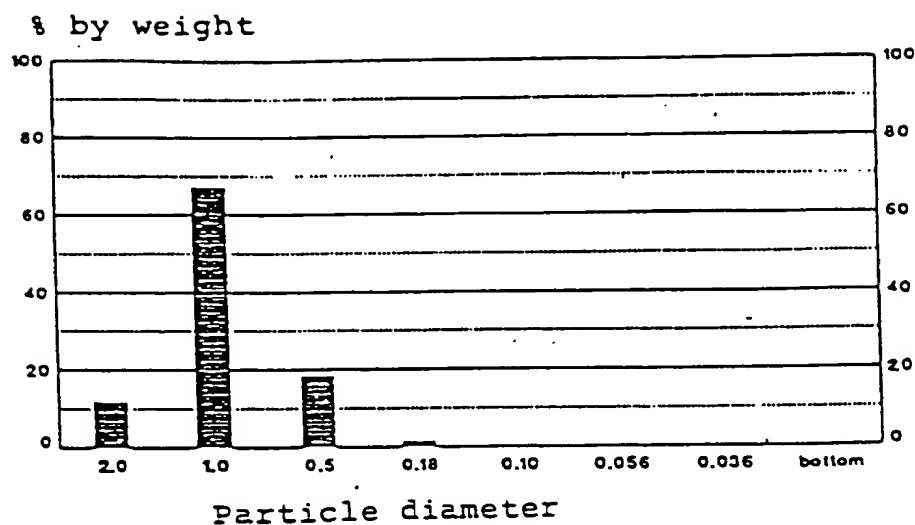


FIG. 14

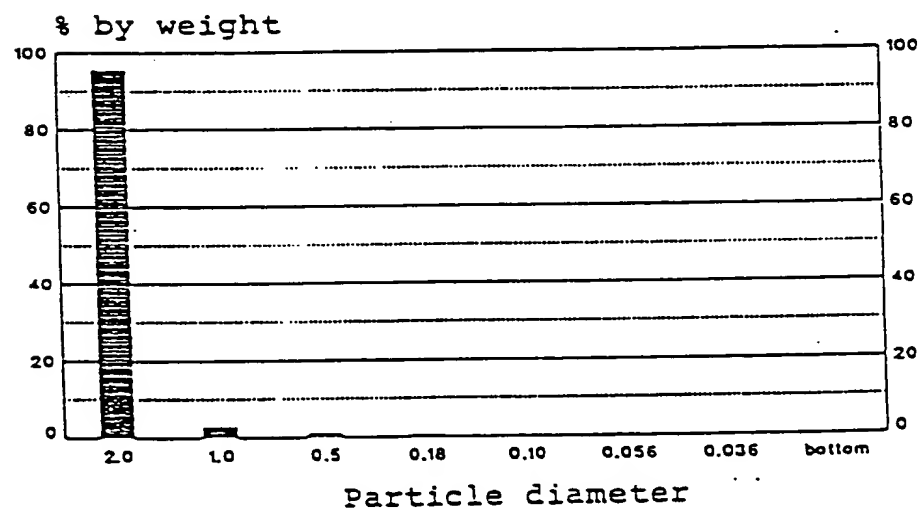


FIG. 15

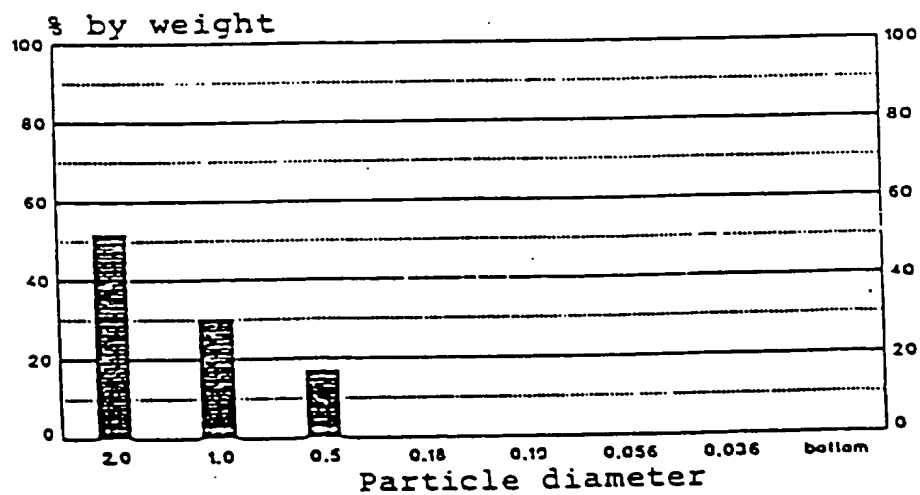


FIG. 16

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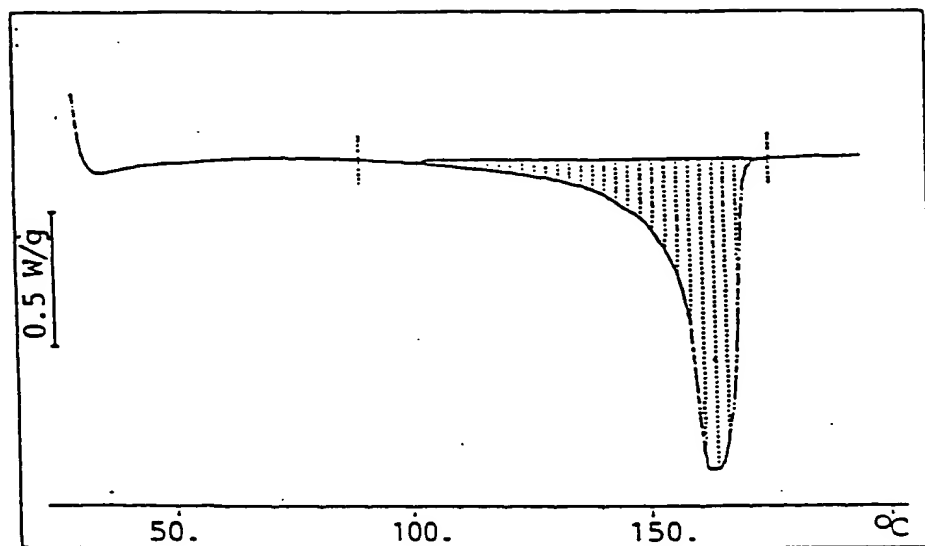


Fig. 19

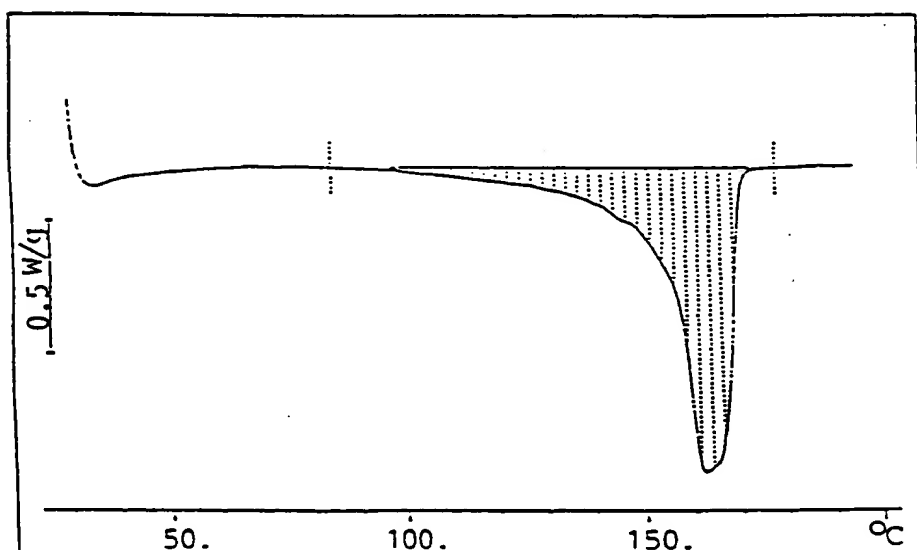


Fig. 20

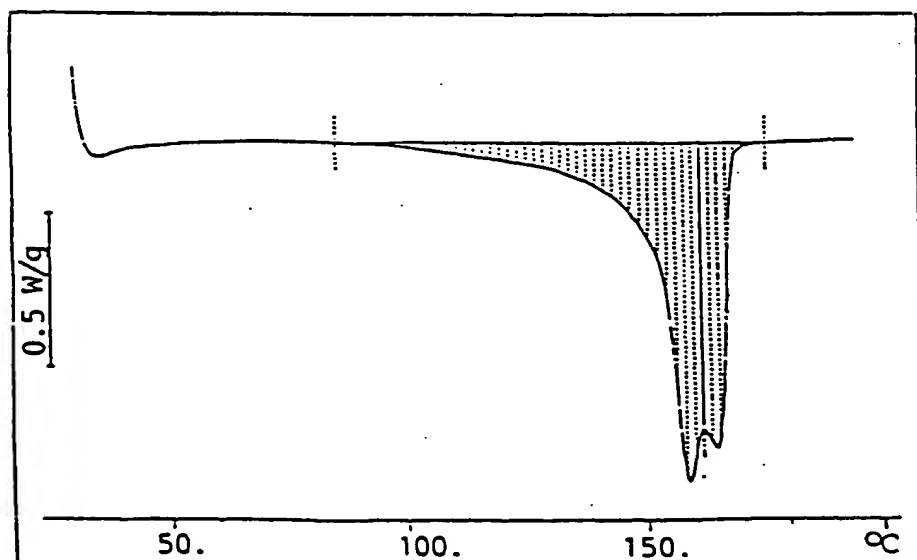


Fig. 21

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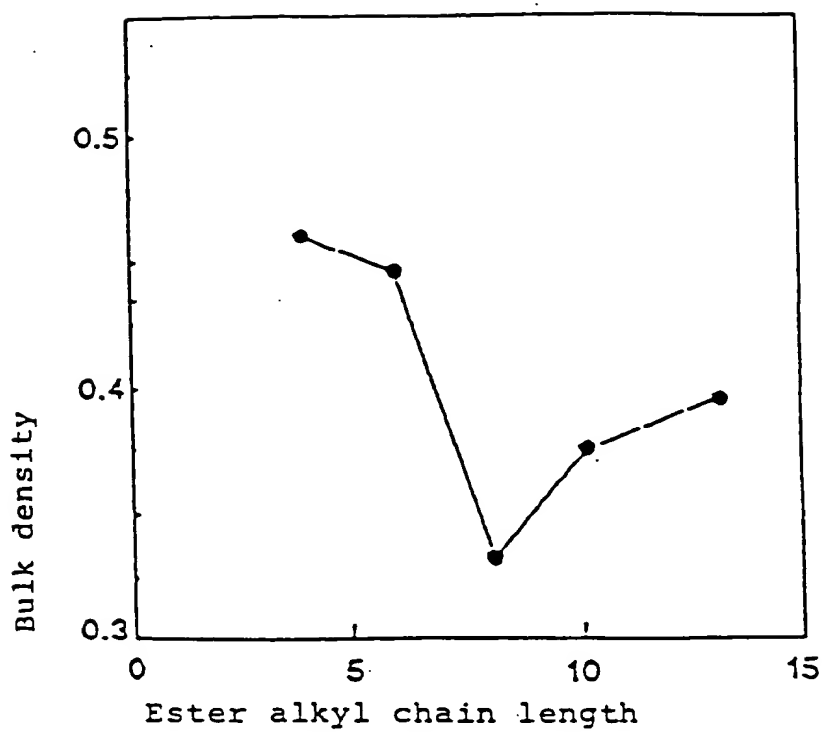


FIG. 18

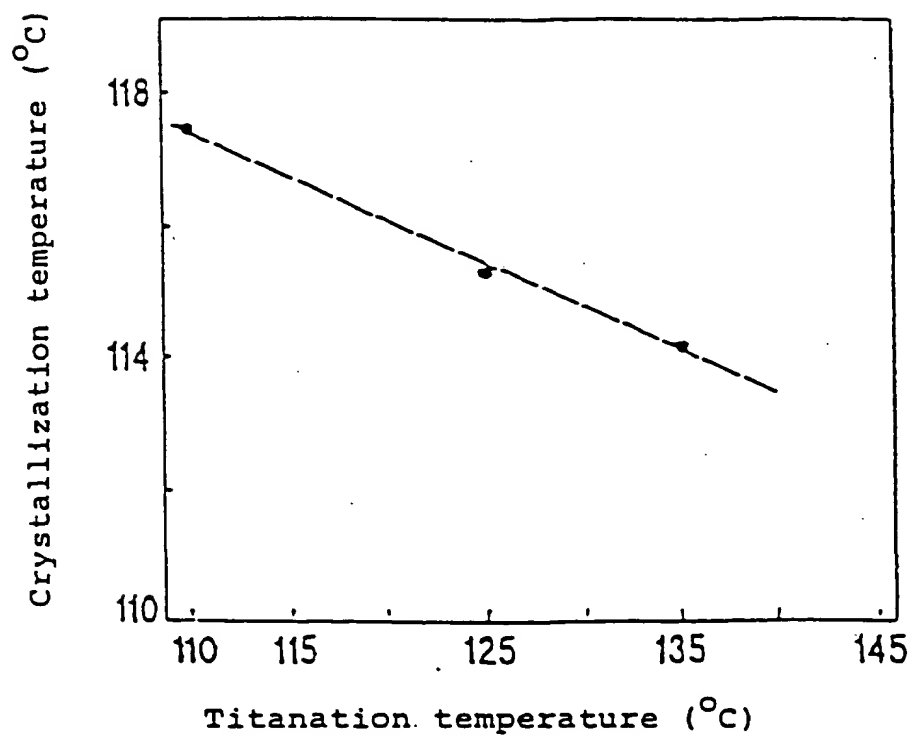


FIG. 22

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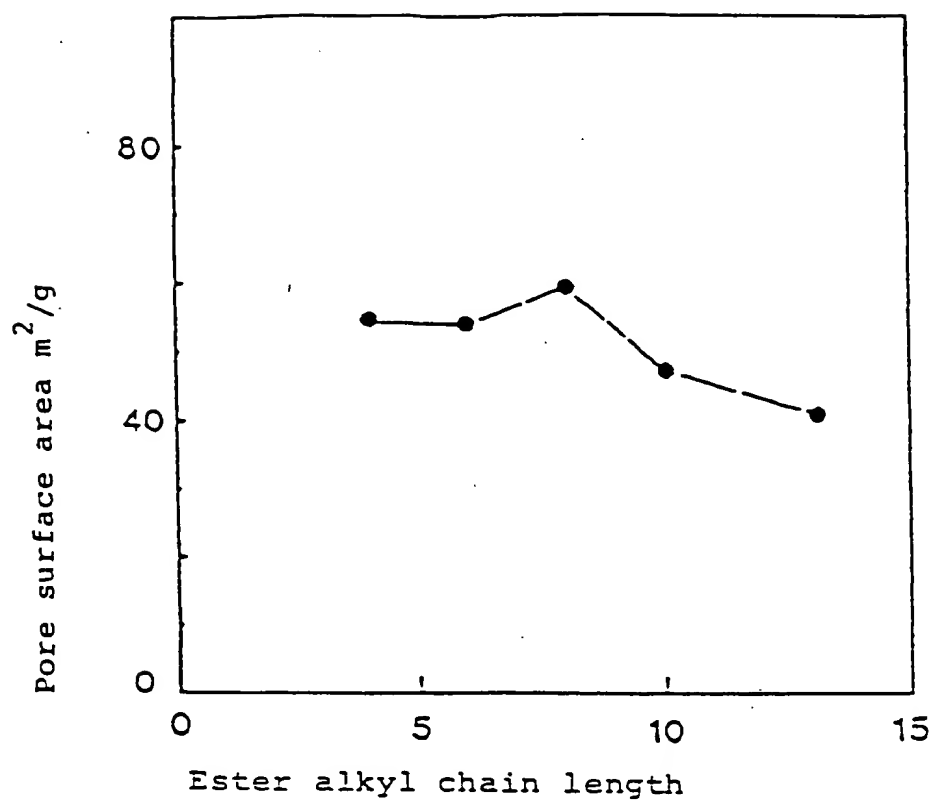


FIG. 23

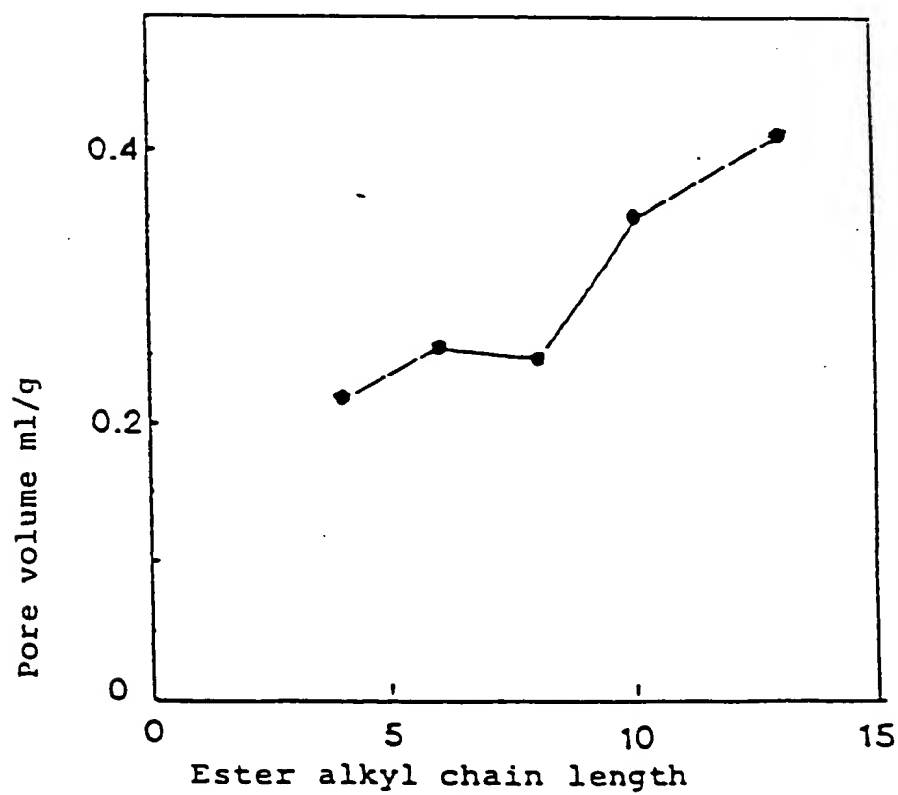


FIG. 24

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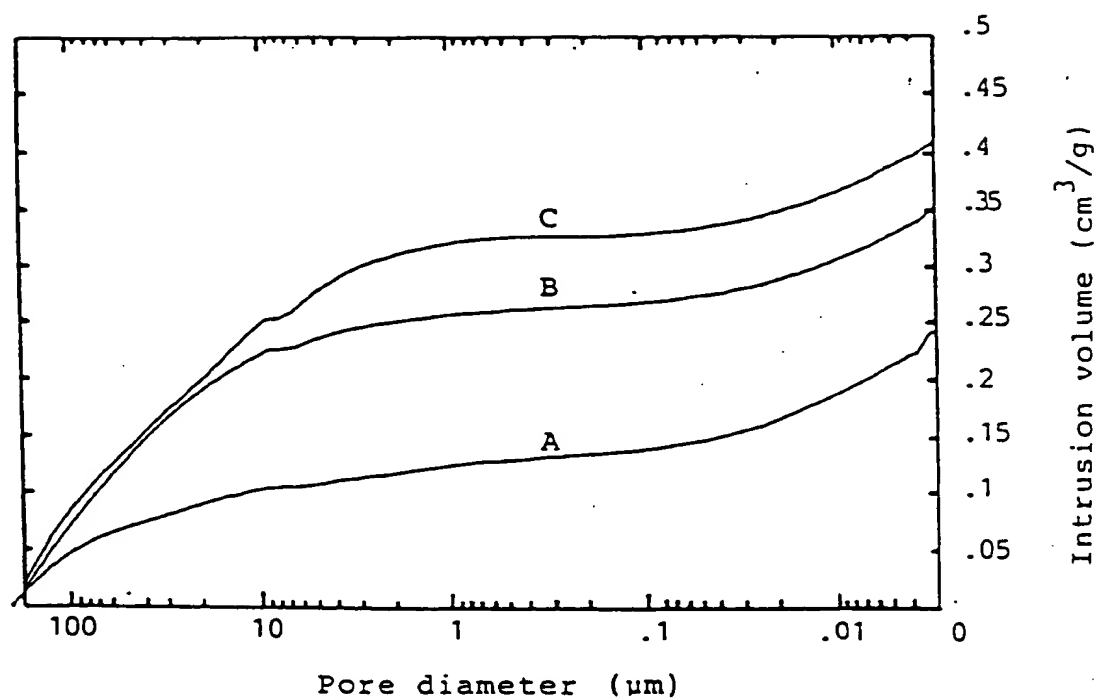


FIG. 25

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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/FI 92/00081

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